

Portable Sensor for Hazardous Waste

Lawrence G. Piper (e-mail: piper@psicorp.com, phone: (508) 689-0003)

Amy J. R. Hunter (e-mail: hunter@psicorp.com, phone: (508) 689-0003)

Mark E. Fraser (e-mail: fraser@psicorp.com, phone: (508) 689-0003)

Steven J. Davis (e-mail: davis@psicorp.com, phone: (508) 689-0003)

Physical Sciences Inc.

20 New England Business Center

Andover, Massachusetts, 01810-1022

Introduction

We are part-way through the second phase of a 4-year program designed to develop a portable monitor for sensitive hazardous waste detection. The ultimate goal of the program is to develop our concept to the prototype instrument level. Our monitor will be a compact, portable instrument that will allow real-time, *in situ*, monitoring of hazardous wastes. This instrument will be able to provide the means for rapid field screening of hazardous waste sites to map the areas of greatest contamination (see Figure 1). Remediation efforts can then focus on these areas. Further, our instrument can show whether cleanup technologies are successful at reducing hazardous materials concentrations below regulated levels, and will provide feedback to allow changes in remediation operations, if necessary, to enhance their efficacy.

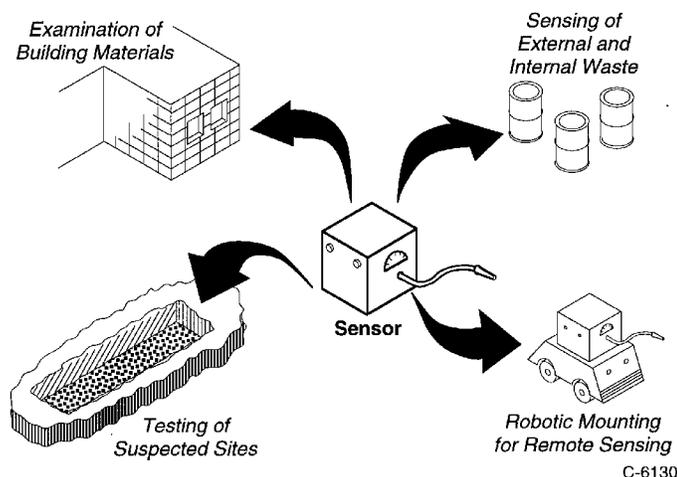


Figure 1 Hazardous waste screening using ANET

Our analysis approach is to excite atomic and molecular fluorescence by the technique of active nitrogen energy transfer (ANET). The active nitrogen is made in a dielectric-barrier (D-B) discharge in nitrogen at atmospheric pressure. Only a few emission lines or bands are excited for each hazardous species, so spectral resolution requirements are greatly simplified over those of other spectroscopic techniques. The D-B discharge is compact, 1 to 2 cm in diameter and 1 to 10 cm long. Furthermore, the discharge power requirements are quite modest, so that the unit can be powered by batteries. Thus an instrument based on ANET can readily be made portable.

During the first phase of the program we demonstrated that a variety of hazardous species could be detected by the technique of ANET excitation of atomic and molecular fluorescence. Species investigated included heavy metals, Hg, Cr, and Se, both chlorinated and non-chlorinated organics, and uranyl compounds. For most of these species we demonstrated sensitivity limits for their detection at parts per billion (ppb) levels.

Our principal goals for this second phase of the program are to develop and breadboard test instrument components and to design a prototype instrument suitable for construction and evaluation in the final phase of the program. A secondary goal is to extend the ANET technology to encompass a greater number of hazardous species, primarily additional heavy metals and radionuclides.

The major problem to overcome in this second phase of the program is to develop procedures for sample handling and analysis. We established ANET as a very sensitive detection technique, but the problem of extracting samples quantitatively, and transporting them to the ANET discharge region is a difficult one. We have settled on a system which uses a small, compact solid-state laser to ablate material from the samples. The throat of our laser-delivery system also houses the D-B discharge used to generate the active nitrogen. Thus, the ANET excitation takes place directly in the sampling region. Light from the discharge is then transported to an optical multichannel analyzer where it is detected. The whole analytical process will be run under control of a small portable computer, and all procedures and processes will be automated.

A second element of the program is to demonstrate sensitive detection of additional species not addressed in the program's first phase. Initially we investigated several species in the gas phase, and were able to establish sensitive detection of Pb, Sb, and As at sub parts per billion levels. It became apparent, however, that our system did not work nearly as well as we had anticipated when the sample was in the form of particulates. We needed, therefore, to be able to vaporize the samples (most of which will be initially in solid or particulate form) prior to the ANET detection process. We developed a system to vaporize these particulates in a high energy, electrically generated spark. With suitable gating between the spark, and the period of fluorescence detection, the spark itself can generate adequate fluorescence to allow aerosols to be identified and detected sensitively. We have demonstrated this system for Cd, Pb, and U so far. We note, however, that using spark fluorescence to detect Pb results in a decrease in sensitivity of several orders of magnitude compared to ANET detection. The spark system requires metal electrodes be exposed directly to the sample. This will cause some problems with proper operation of the D-B discharge in addition to introducing some extra contamination in the form of metal sputtered from the spark electrodes. To alleviate these difficulties, we are currently investigating laser ablation to vaporize our samples. Our preliminary results on Pb are promising.

The final element of this phase of the program is to design a prototype hazardous waste monitor. This design includes not only identifying each of the components to be incorporated into the instrument and determining how they will be integrated into a compact package, but also specifying component technical requirements and their vendors. This design process will begin around the new year, and will be the primary focus during the final months of the program's second phase. At the end of this current phase we will have a detailed set of drawings and

specifications for the construction of a first-generation, or alpha-, prototype instrument. This instrument will be built and field tested as part of the third and final phase of the program.

The third, and final, phase of the program will involve fabrication and field testing of the alpha-prototype instrument designed during the program's second phase. We will test and refine the instrument in the laboratory first, then conclude the program with an extensive series of field tests.

Approach

The technique we chose for detecting hazardous species with high sensitivity was excitation of atomic and molecular fluorescence by ANET. The active nitrogen is made in a D-B discharge in nitrogen at atmospheric pressure. Figure 2 illustrates our instrument concept schematically. Samples, ablated from the contaminated surface and vaporized in a laser pulse, flow into the D-B discharge region where the active nitrogen is generated, and where it transfers its energy to species in the sample, thereby exciting fluorescence from them.

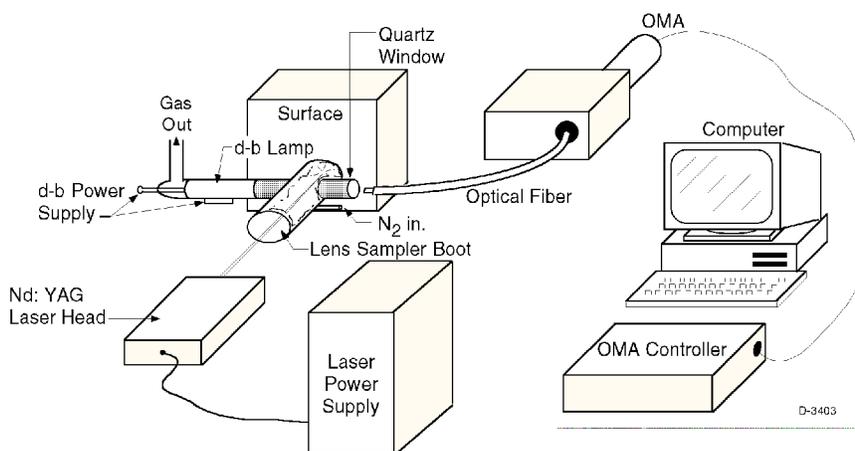


Figure 2 Schematic of analysis system integrating LIBS sampling with ANET detection

The pertinent fluorescence is then isolated by a small spectrograph and is detected by a photomultiplier or diode array placed in the spectrograph's exit plane. Signals from the detector are then processed by a computer and a report is generated. The computer control allows both real-time reporting and data storage for subsequent processing or archiving.

ANET excitation generates only a few emission lines or bands for each hazardous species (see Fig. 3). Thus, spectral resolution requirements are greatly simplified over those of other spectroscopic techniques. The D-B discharge is compact, 1 to 2 cm in diameter and 1 to 10 cm long. Furthermore, the discharge power requirements are quite modest, so that the unit can be powered by batteries. Thus an instrument based on ANET can readily be made portable.

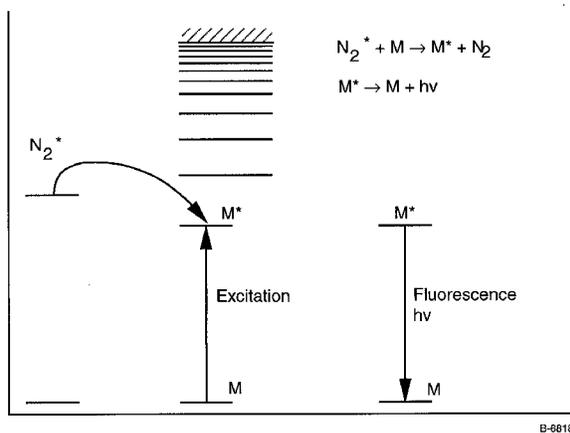


Figure 3 ANET Excitation Mechanism

Active Nitrogen Energy Transfer (ANET)

From the beginning of this century, scientists have observed characteristic emissions from atoms and free radicals when atomic and molecular species were added to active nitrogen. A rich literature exists detailing the chemical reactions and energy-transfer processes that occur to excite these emissions.¹⁻⁶ Basically, metastable nitrogen molecules (molecules having internal energies of about 6 eV which they cannot easily release via radiation) in the active nitrogen transfer their energy to the various acceptor species. These acceptor species then fluoresce at wavelengths characteristic of the acceptor. Most of these studies relied upon the recombination of nitrogen atoms at relatively low pressures to generate the metastable nitrogen molecules. For analytical applications, this approach has the disadvantage that considerable power is required to dissociate atomic nitrogen. In addition, because these systems operate at pressures on the order of 1 to 10 Torr, a vacuum system is required and sampling under ambient conditions becomes much more difficult.

We conceived and began developing ANET as an alternative to active nitrogen analytical techniques using an atomic-nitrogen recombination source. Our approach is to generate the metastables in a D-B discharge operating at atmospheric pressure and total powers of a few Watts. Thus our system requires neither a large power source nor a vacuum system. In addition, we believe that the overall metastable number densities generated in the D-B discharge are several orders of magnitude larger than those in the atom-recombination system, which means that ANET has the potential to be several orders of magnitude more sensitive.

Dielectric-Barrier (D-B) Discharge Technology

A D-B discharge is a high voltage a.c. discharge between two electrodes, at least one of which is separated from the discharge region by a dielectric-barrier (D-B) (insulator) such as glass⁸⁻¹¹ (see Fig. 4). A typical discharge will run at voltages between 3 and 30 kV at frequencies from line frequency to 100 kHz. Gas pressures are typically an atmosphere and gap spacings are on the order of a few millimeters. In its simplest form, the discharge can be powered by attaching the electrodes to the output of a high voltage, step-up transformer, such as a neon-sign transformer, plugged into a variac.

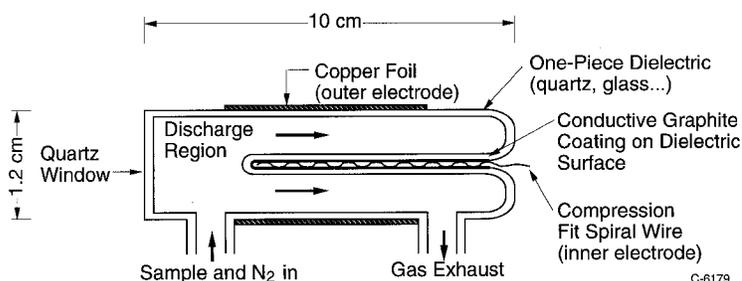


Figure 4 Dielectric-Barrier Discharge Lamp

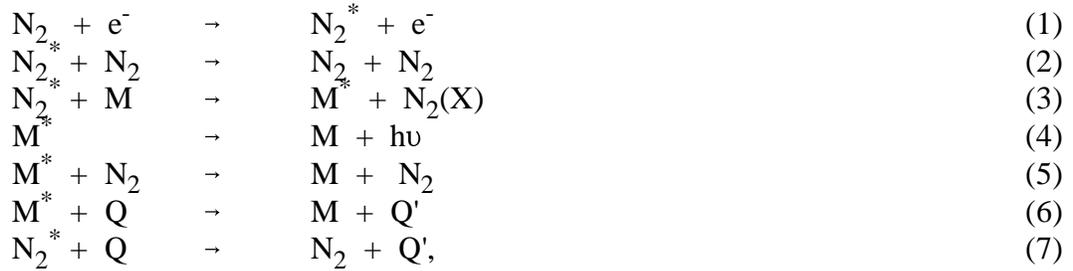
The D-B discharge (also referred to as an ozonizer discharge) is not a single discharge in the sense of a continuous arc or glow discharge, but rather a collection of innumerable microdischarges between the dielectric and the other electrode. These microdischarges consist of short duration (typically 10 to 100 ns) current pulses (100 to 1000 A cm⁻²) localized in roughly cylindrical filaments, typically 100 μm in radius. The mean electron energy in a microdischarge is

on the order of 1 to 10 eV which is ideal for metastable generation. At any given instant in time, the microdischarges are distributed uniformly across the face of the dielectric. This uniformity provides a relatively stable excitation throughout the discharge volume.

The Chemistry and Physics of ANET

D-B discharges in pure nitrogen have been shown to be efficient sources of metastable $N_2(A \ ^3\Sigma_u^+)^{12-15}$, even at pressures of one atmosphere, thus providing the active nitrogen source necessary for the selective analyte excitation of ANET. If the analyte species is an atom, such as elemental mercury or lead, the excitation occurs directly. When molecular species are added to the discharge region, the $N_2(A)$ generally reacts with the molecule, producing molecular fragments, which it subsequently excites. For example, $HgCl_2$ is dissociated to $HgCl^*$ which emits around 540 nm, organic molecules are broken down into CN radicals which emit near 388 and 420 nm, and chlorinated organics to CCl molecules emitting at 278 nm.

The chemical processes responsible for exciting fluorescence from species M in a D-B discharge are summarized by the following reactions:



where, Q represents a species in the discharge that quenches electronic energy in either the N_2^* or the electronically excited analyte fragment.

Although the D-B discharge is a pulsed discharge, one can treat it as if it were a continuous discharge if observations are averaged over a number of discharge cycles. Then, because of their short radiative and quenching lifetimes, the excited species in the discharge region are effectively in steady state and we can write

$$I_{M^*} = k_4[M^*] = k_3[M][N_2^*]/(1 + (k_5/k_4)[N_2] + (k_6/k_4)[Q]). \quad (8)$$

Equation (8) shows that for constant metastable number density and total pressure, the fluorescence intensity will be linearly proportional to the additive number density, provided the number densities of any potential quenchers remain constant. This generally will be the case. In previous investigations, the linearity of active-nitrogen excited fluorescence intensity with analyte number density has been demonstrated experimentally to cover four to five orders of magnitude for many species.

The exciting species in active nitrogen responsible for exciting fluorescence from additives generally is considered to be $N_2(A \ ^3\Sigma_u^+)$, although other nitrogen metastables have been invoked

from time to time.¹ $N_2(A)$ carries about 6 eV of internal energy. Based on the reaction scheme above, its effective steady-state number density is given by

$$[N_2^*] = k_1[e^-][N_2]/(k_2[N_2] + k_3[Hg] + k_7[Q]). \quad (9)$$

The radiative lifetime¹⁶ of $N_2(A)$ is about 2.5s. Thus, the primary mechanism for its deactivation will be quenching rather than radiative decay.

Quenching of either the analyte fluorescence or the nitrogen metastables can be an issue affecting the sensitivity of ANET. Although rate coefficients for quenching $N_2(A \ ^3\Sigma_u^+)$ and many analyte emissions by a number of important species are known,^{7, 17-19} one should determine the effects of quenching in a D-B discharge *in situ* to ensure that unexpected processes do not complicate the analysis. Our observations related to metastable nitrogen quenching in the D-B discharge²⁰ are generally consistent with more direct quenching measurements. While our Phase A investigations showed air quenching could be a problem in our system, we shall be able to circumvent this particular complication in the present situation by performing our ablation/ excitation in a nitrogen atmosphere. That is, we will first flood the surface being tested with pure nitrogen prior to sampling so we may exclude oxygen from the surface.

Project Description

Summary of Phase A Results

The primary goals of the first phase of the program were two fold:

- to demonstrate the variety of hazardous species that can be detected by the technique of ANET excitation of atomic and molecular fluorescence;
- to demonstrate that sensitivity limits for detecting several of these species are at parts per billion (ppb) levels.

Species to be investigated included heavy metals, organics and chlorinated organics, and/or trans-uranic surrogates.

To achieve the stated Phase A goals, we designed a program where we first focused on the ANET technique by studying parameters important to the production and quenching of nitrogen metastables in an atmospheric pressure, D-B discharge. These metastables are the primary excitation species in the active nitrogen. The second component of the program was qualitative and quantitative studies on the detection of several hazardous species including heavy metals, both chlorinated- and non-chlorinated-organic molecules, and uranium compounds. The third component of the program was to investigate the effects of adding small quantities of dust to the D-B discharge region. The two issues to be resolved in this part of the investigation were whether the presence of dust in the discharge region would compromise the operation of the D-B discharge and whether species adhering to dust could be detected.

We demonstrated a linear relationship between the intensity of the ANET excited fluorescence and the concentration of the additive in the discharge region for detection of the heavy metals Hg, Cr, and Se. Our results indicated a sensitivity for Hg and Se detection below 1 ppb. The sensitivity for Cr detection appeared to be somewhat higher, and we have reinvestigated this species during the current phase of the program

All hydrocarbons studied can be detected in a D-B lamp in nitrogen at atmospheric pressure by observing emission from the CN(B - X) system at 388 or 420 nm. Furthermore, if the hydrocarbon is chlorinated, one observes CCl emission at 278 nm in addition to that from CN. The relationship between the mole fraction of added hydrocarbon and CN or CCl band intensity was also linear, and sensitivities at both wavelengths were at the parts per billion level.

Adding Uranyl compounds to the discharge region resulted in the appearance of three rather broad bands appearing at 486, 510, and 534 nm in the spectrum. We think these spectral features indicate uranium oxide excitation in the D-B discharge, probably UO_2 , but possibly UO.

Objectives of Phase B Program

The work in the first phase of this program successfully demonstrated that ANET technology holds great promise for development into a sensitive, multi-element hazardous species monitor. Our plans for the second phase of the program are to develop a breadboard prototype system and characterize the ANET process under more realistic conditions. During the third phase we will build a working prototype of a commercial instrument and test it in the field.

The Phase B program has three primary components:

- process development
- design engineering
- technology extension.

The purpose of the process development task is to establish the procedures for sample handling and analysis, and to develop systems and software needed to automate these processes. System components and processes to be examined include sample collection and introduction, active nitrogen source stability, fluorescence detection and analysis, and measurement, calibration, and test procedures.

The most crucial issues are sampling, calibration, and testing. The other issues, fluorescence detection and analysis, active nitrogen source stability, and measurement procedures, were explored in some detail in Phase A. Implementing these components into the breadboard system will be straightforward.

The sampling and testing issues, however, will ultimately determine the success or failure of the ANET technology. Designing a system that abstracts samples truly representative of the hazardous environment is crucial. Only if this is accomplished can the true hazardous species

concentrations be determined accurately. Therefore, sample entrainment, speciation, calibration and matrix effects are of primary import.

The design engineering task has two elements. The first of these is to identify and specify each of the components to be incorporated into the prototype instrument we shall fabricate as a part of the final phase of the program. Each component needed will be enumerated, and commercial suppliers will be identified. We will investigate the efficacy of in-house construction of some components versus their purchase from commercial OEM suppliers. Final component suppliers will be determined by balancing various factors, including adaptability, quality, size, weight, and cost.

The second element of the design engineering task is to design a prototype hazardous waste monitor. This design will balance a number of considerations including power management and portability. The location of each component will be studied in relation to the others to identify configurations that promote simple operation and servicing while retaining compactness in the whole instrument. At the end of the program's second phase we will have a detailed set of drawings and specifications for the construction of a first-generation, or alpha-, prototype instrument.

The third component of the program is to demonstrate the applicability of the ANET technology to detecting a number of hazardous species not investigated in Phase A. The activities on this task will involve not only identifying unique finger prints for each of the species to be investigated, but also to determine quantitative limits for their detection. The species we shall investigate in this task include the heavy metals, Sb, Be, Cd, Cr, Pb, and Hg, and the radionuclides, Tc, Th, and U.

Results

This section outlines our progress to date on the process development, engineering development, and technology extension tasks. Our major focus to date has been on solving the problems related to sampling and on extending the technology to additional heavy metals. Before describing the results of our activities on these tasks in detail, however, we begin by describing our basic concept of an ANET-based hazardous waste sensor.

Process Development Tasks

An instrument using ANET to monitor hazardous wastes in real-time will have five essential components:

1. a sampling system for collecting the sample from contaminated material, mixing it with nitrogen, and transporting it to the discharge region;
2. a discharge system for exciting the N₂ metastables which, in turn, excite contaminant fluorescence;

3. a detection system for separating contaminant fluorescence from other features excited either in the discharge or by the N₂ metastables;
4. an *in-situ* calibration system to ensure the accuracy of the hazardous waste measurements; and
5. a data processing system for controlling the various instrument components, for collecting the data, for converting the raw data into hazardous waste concentrations in the sample, and for reporting and archiving hazardous waste analysis results.

In our developmental work, we considered each of these issues in some detail before beginning to purchase and assemble components.

We will begin by describing the basic principles of the instrument operation. Figure 2 (above) shows a block schematic of the instrument where the component subsystems are identified. The surface to be tested is first flooded with pure nitrogen to eliminate oxygen from the system. Then the sample is removed from the surface and transported in a flow of nitrogen to the discharge system. In the discharge chamber, the N₂ metastables, and subsequently the contaminant fluorescence, are excited. Light from the discharge is dispersed by a small monochromator and detected with a photomultiplier or intensified photodiode array. The detected signals are read and processed by a computer system, and results are displayed and stored. The computer system can also provide feedback signals for active control of remediation processes.

A calibration system will be included that can inject known quantities of contaminant into the diluted sample flow prior to its entry into the discharge cell. In addition, we will be monitoring an emission feature of the discharge that is diagnostic of the N₂ metastable number density. This allows for correction of the fluorescence data for variations in excitation strength either because of pulse-to-pulse variations in discharge strength or because of residual quenching of the metastables by impurities remaining in the sample stream.

Our initial system performance and design goals are as follows:

- ability to detect heavy metals and radionuclides in gas phase and on particulates
- sensitivity range for all species below OSHA limits
- automatic, *in situ* calibration of all contaminant species
- analysis and display of results in less than one minute
- size, <50 x 50 x 100 cm (ca. 10 ft³)
- weight <75 kg
- power <1.5 kilowatts.

Sampling system. Our initial focus is the detection of contaminants adhering to building materials or other surfaces. While ANET is a sensitive technique for air-borne species, such species must first be liberated from the surface into the gas phase and then transported to the discharge region. In some instances, the contamination might lie on the surface to be sampled in the form of dust particles. In other instances, however, the contamination might be closely bonded to the surface either as a component of a surface coating, e.g., paint, or even trapped beneath a surface coating.

We can think of three primary methods for removing contamination layers of material from a surface that might prove suitable for the present application. Mechanical means for sample removal from surfaces might include miniature impingers, somewhat along the idea of a small jackhammer, or abrasive removal, e.g. via a jet of solid CO₂ pellets. A second means of sampling would be to ignite an electrical spark at the surface which would remove material either through generating heat from the spark-induced plasma, or from a shock-wave created by the spark. A third method, somewhat related to the second, would be to use a laser to ablate material from the surface.

Using mechanical means for sample extraction will result in a sample that is essentially an aerosol. The other two techniques described above will result in a sample that is a mixture of vapor and fine particulate. In the first phase of this program, we showed evidence that ANET was not seriously compromised by the presence of some fine particulate in the discharge region. Our results seemed to indicate further that the ANET microdischarges themselves might be potent enough to vaporize some of the particulate in the discharge region. We have since found that the ANET discharge is not generally suitable for detecting species adhering to particulates. Since electrical and laser ablation of the sample both can provide some of the sample in the vapor phase, one of these two approaches appears to be viable.

Our examination of the benefits and liabilities of these two latter approaches indicates that laser ablation appears to offer the most reproducible and compact method for sample extraction. We have found a miniature Nd:YAG laser can readily ablate paint that contains lead from concrete blocks. The laser is about half the size of a shoe box, and produces output pulses at a rate of 10 Hz. The laser plasma itself contains emissions from the added contaminant. Examining laser-induced plasmas for diagnostic emissions is commonly known as laser-induced breakdown spectroscopy or LIBS. Generally, LIBS systems use a much larger laser than the one we have been using, and they generally require a much more sophisticated detection system than what we have been using. In addition, LIBS systems tend to be much more expensive than ANET based systems, and significantly less sensitive. Thus, we think that incorporating an ANET detection system with a laser-based ablation system offers the greatest potential for sensitivity, compactness, and limited cost.

Figure 2 (above) shows the hybrid laser-ablation/ANET system schematically. The laser is fired through a lens at the end of the sample tube. The other end of the sample tube seals the surface to be tested with an o-ring. A flow of nitrogen sweeps into the sampler at the gas surface and purges air from the region. The nitrogen flow exits the sampler through a D-B discharge lamp that has been attached to the sampler. Opposite the D-B lamp is a quartz window so that

the D-B discharge emission can be observed. Light from the D-B lamp is collected by a fiber-optic bundle and transported to an optical multichannel analyzer (OMA) where the light is dispersed and subsequently detected.

Detection system. The detection system monitors contaminant fluorescence, primarily at ultraviolet wavelengths, and N₂ Herman infrared (HIR) fluorescence between 695 and 710 nm. We showed in the Phase A program that the HIR fluorescence can be related directly to the concentration of N₂ metastables produced in the discharge. Monitoring the HIR emission, therefore, provides a means of compensating for variations in metastable concentrations that might occur with variations in air in the sample or with pulse-to-pulse irregularities in the D-B discharge itself. The spectral resolution necessary to separate the atomic fluorescence from neighboring emissions in the D-B discharge is about 0.4 nm, about an order of magnitude less than required in commercial ICP or LIBS systems. Spectral resolution requirements in the near infrared are less stringent, so using an interference filter at 700 nm may be useful. A spectrometer is necessary to obtain adequate spectral resolution in the ultraviolet, however, and works well to isolate other important wavelengths.

A compact spectrometer having a 10 to 15 cm focal length and a standard 1200 g mm⁻¹ has a first-order resolution of about 8 nm mm⁻¹. Since aberrations in small focal length spectrometers limit their usefulness to slit widths greater than 100 to 150 μm, the best first-order resolution one can expect is about 1 nm. Adequate resolution is therefore readily available using a somewhat higher density grating (1800 to 2400 g mm⁻¹) with fluorescence monitoring in second or third order. Such spectrometers are readily available with computer-controlled, stepper-motor based grating rotation mechanisms have been made sufficiently rugged to withstand the rigors of space flight. A computer-controlled filter wheel situated at the monochromator's entrance slit enables switching between filters appropriate to the spectral region observed. The system collects data from a few discrete wavelengths in a spectral region; then slews to the next wavelength region and repeats the procedure. A UG-5 glass filter adequately transmits ultraviolet radiation with wavelengths longer than about 225 nm while completely blocking that at wavelengths between 400 and 650 nm. For visible wavelengths, a long-pass colored glass filter effectively blocks second-order uv radiation while transmitting that at longer wavelengths.

A compact photomultiplier assembly detects fluorescence at the exit slit of the monochromator. Emissions from the discharge extend for a period of tens of nanoseconds after the initiation of the discharge pulse if they are excited directly in the discharge, but will extend up to 100 to 200 μs if excited by metastable transfer. To enhance discharge emission relative to dark current the photomultiplier's output is integrated for periods of about 150 μs after the discharge pulse. The data acquisition system then reads the voltage output of the integrator and averages the result with those of a number of previous pulses.

Discharge system. Our discharge system is similar to that used previously.²¹ It is powered by applying 15-volt, square wave pulses to a high-energy induction coil. The discharge frequency is controlled by one of the data acquisition and control system's timers. Digital pulses from the computer trip a gate, which in turn, opens a transistor switch able to sink adequate levels of current at 15 Vdc to the coil's primary. The high-voltage output of the coil's secondary

connects to the D-B discharge lamp. We have found this system to be compact and quite rugged and reliable in operation.

Data acquisition and control system. The data acquisition and control system regulates all components of the hazardous waste sensor, collects data from each component, runs automatic system calibrations, converts collected data into contaminant-species concentrations, and displays measurement results in real time as well as stores them for later retrieval and archiving. For the current program prototype, we are using a portable computer for this purpose. A commercial instrument would undoubtedly incorporate a single-board computer with operations programmed into EEPROM memory.

Our system uses an IBM-compatible portable PC with Windows 95-based software. Several data acquisition and control boards are installed inside the computer. Software to monitor and control the boards is being developed using the National Instruments LabView, object-oriented programming language. This system produces a virtual instrument that has a screen display much like an instrument panel. It is controlled from the screen by clicking mouse the computer's mouse on virtual buttons, or by entering numbers into specially designated blocks on the screen. An example of one of our instrument panels is shown in Fig. 5.

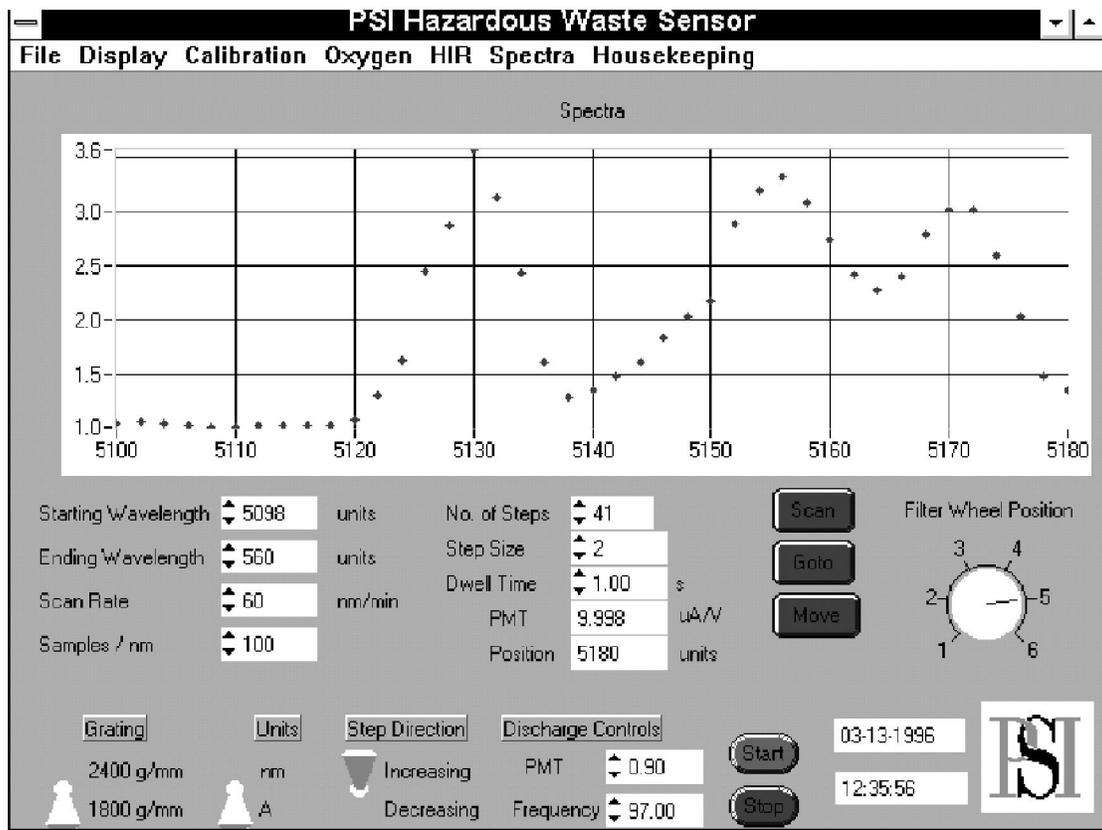


Figure 5 Virtual instrument control panel created with LabView programming

Technology Extension Tasks

Activities on this task follow procedures developed during the first phase of the program. The main purpose of this task is to establish sensitivities for detecting additional hazardous species that were not addressed in the first phase of the program. The list of species includes the heavy metals, Sb, Be, Cd, Cr, Pb, and Hg, and the radionuclides, Tc, U, and Th. For some of these species, we investigated their detectability using volatile compounds, such as tetraethyl lead, and chromium hexacarbonyl. The techniques used in these studies are virtually the same as those described in detail previously.²² We will therefore only mention the results of the measurements below in the results summary.

We do not think, however, that our sensor will be required only to analyze gas phase samples. In fact, we expect that most samples will exist as aerosols. The majority of metallic compounds do not have an appreciable vapor pressure, and exist primarily as solids, either aerosol particulates or the more familiar large scale solid material. Our initial indications were that the ANET system would be able to detect species bound up as aerosols. Our more detailed investigations of this process, however, indicated quite the opposite: in general, the ANET technique does not handle detection of species bound up as aerosols adequately. We therefore needed an alternative technique that was suitable for such situations. The technique we employed for such diagnostic measurements is spark-induced breakdown spectroscopy, or SIBS. To date, we have used SIBS to demonstrate sensitive detection of aerosols containing compounds of Pb, Cd, and U

Experimental details of SIBS

measurements. The aerosol generation-spark excitation system has three main sections: the droplet generator, the drying column and the spark chamber. The droplet generator is a variant on the design first demonstrated by Berglund and Liu²³ and is shown in Fig. 6. The operating principle involves the imposition of a periodic instability on a thin stream of fluid flowing from a pinhole orifice. The instability is induced by coupling a single frequency vibration into the fluid using a piezoelectric transducer driven by a square wave function generator. Under certain conditions of fluid flow rate and instability frequency, monodisperse aerosols are generated.

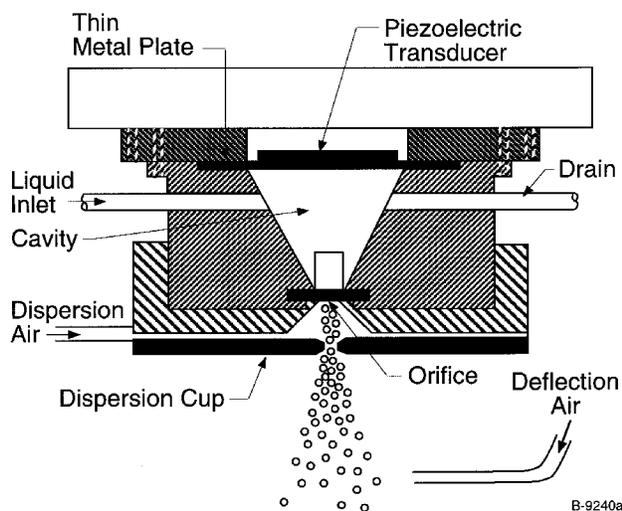


Figure 6 The monodisperse droplet generator

The size of the droplet is a function of the instability frequency and fluid flow rate through the orifice:

$$D_p = \left(\frac{6Q}{\pi f} \right)^{\frac{1}{3}} \quad (10)$$

in which Q is the fluid flow and f is the frequency. For previous studies done with this generator, a frequency of 100 kHz and a flow rate of 0.34 ml min^{-1} was used to produce droplets $48 \mu\text{m}$ in diameter. The fluid flow itself is a function of orifice size. Typically we use orifices that are $20 \mu\text{m}$ in diameter.

This droplet generator is situated at the top of a Plexiglas tube in a downward directed orientation toward the drying column (Fig. 7). Loss of particles in the drying column walls is minimized by the use of a porous stainless steel inner tube through which air is drawn at a fixed rate. The air is heated to 100°C to facilitate removal of water from the droplets and is drawn out the bottom of the column by a filtered pumping system. The dry aerosol is trapped on a filter placed at the bottom of the Plexiglas extension that houses the spark chamber. This filter prevents particles from exiting the generator and contaminating the laboratory environment.

At the bottom of the drying column lies the spark chamber, which houses the electrodes. Rhenium electrodes have been used previously because of their resistance to oxidation and arc corrosion, and also due to their high melting point (3180°C). The electrodes are mounted directly to stainless steel blocks which are in turn mounted on ceramic standoffs inserted into the sealed aerosol source. The chamber has arms with windows at the ends to pass the emission generated upon sparking. The detection system (monochromator and OMA) relies upon a timing system which allows the analysis of the atomic emission after a delay to eliminate interference from the prompt spark-plasma emission.

The spark is generated by a power supply external to the chamber. The power supply provides the energy for the discharge and a method of synchronizing the discharge with external signal processing and timing electronics. This circuit initially generates short, low-energy, high-voltage sparks across the electrodes in the same fashion as those produced on the spark plugs of an automobile engine. These pre-ignition sparks provide a conduction path for the primary capacitor, which is kept charged by a second power supply. Immediately after the high voltage

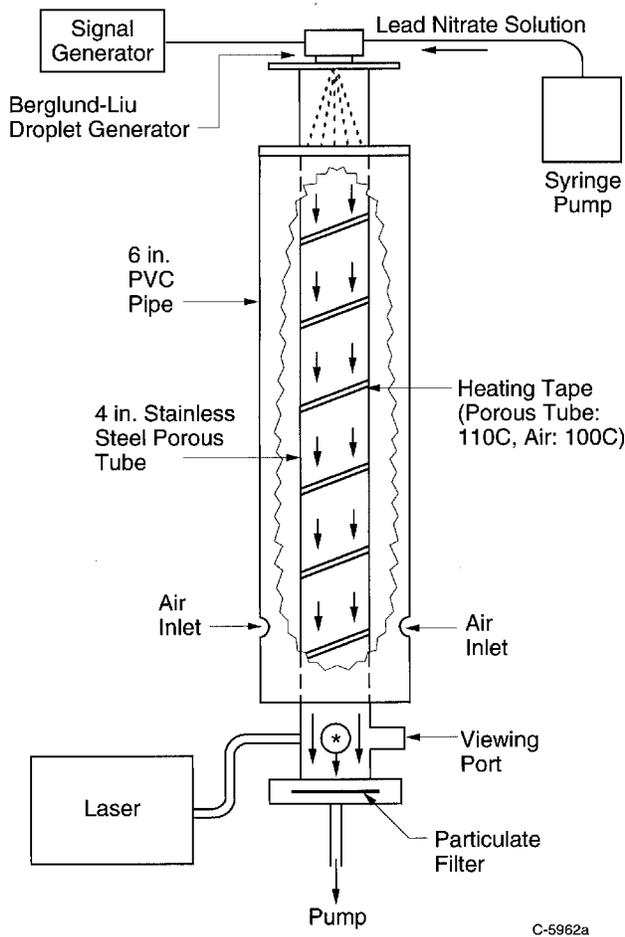


Figure 7 The dry aerosol source, including spark chamber and drying tube

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spark is struck, the primary capacitor discharges, providing the majority of the pulse energy. This pulse energy can be varied from 0.3 to 6 Joules.

In order to calculate the concentration of aerosol in the air, one needs to measure the efficiency with which the aerosol traverses the drying tube:

$$C_{\text{ppmw(air)}} = \frac{M(\text{gm/min}) \cdot E}{F(\text{cm}^3/\text{min}) \cdot \rho(\text{gm/cm}^3)} \cdot 1 \times 10^6 \quad (11)$$

where M is the mass introduction rate, E is the passage efficiency (particle loss in the generator), F is the air flow and ρ is the air density. Under normal operating conditions in the generator, a 1% by weight solution of lead nitrate corresponds to about 50 ppmw (Pb in air). The only component of this equation that is related to the initial concentration of lead is the mass introduction rate. Therefore, to calibrate for other densities, different solution concentrations need to be introduced.

When the dry aerosol is exposed to the spark, it is atomized and excited simultaneously. To avoid errors associated with inhomogeneity in sampling, having a volume-filling spark that samples many particles at once is desirable. Our aerosol source produces sufficient particle densities to ensure the processing of many particles during a spark event:

$$\rho(\text{cm}^{-3}) = \frac{R(\text{s}^{-1}) \cdot E}{F(\text{cm}^3\text{s}^{-1})} \quad (12)$$

where R is the particle generation rate (100 kHz), E is the passage efficiency, and F is the gas flow rate through the system. In a typical experiment, the particle density was about 170 cm^{-3} . A 5 Joule spark transcribes a cylinder that is 7 mm in length and 4 mm in diameter. The corresponding volume is 0.09 cm^3 . Consequently, about 16 aerosol particles were sampled in each pulse. Naturally, sampling many particles not only results in reduced sample inhomogeneity errors, but also in larger signal levels.

Calibration of aerosol delivery system. We calibrated the dry aerosol generator gravimetrically. We describe the process for a lead nitrate, $\text{Pb}(\text{NO}_3)_2$, aerosol. We compare the mass rate at which lead nitrate passes through the particle generator with the mass recovered on a filter at the bottom of the drying tube to determine the efficiency for lead particles to pass through the apparatus.

A high flow filter with a nominal pore size of 1 micron was dried in an oven at 160°C for about half an hour to remove any water absorbed from the atmosphere. The filter was then weighed and introduced into the aerosol generator without the spark chamber, and one of several solutions of lead nitrate was fed through the droplet generator. After enough mass had accumu-

lated on the filter to be easily differentiated from the pre-weight, the filter was removed, heated again to 160° C for half an hour (since the column beneath the droplet generator was heated to 110°C, there was probably not any water remaining, but this step assured that each filter was in the same dry state, before and after). Following the final drying step, the filter was weighed again. The mass difference was then compared with the known amount of lead nitrate introduced into the generator. This ratio is the mass recovery efficiency. Our mass recoveries are uniformly high (0.85 to 0.95), indicating that particle losses within the generator/drying tube are minimal.

Table 1 displays the results of the mass recoveries and the calculations of dry particle diameter and lead concentration. These mass recoveries reproduce the results of prior experimentation at PSI very well.

Table 1. Results of Aerosol Mass Recovery Tests

Solution Concentration (% wt)	Mass Recovery Efficiency	Dry Particle Diameter (microns)	Lead Concentration (ppmw in air)
0.091	0.95	4.6	8.6
0.41	0.90	7.6	36.2
0.41	0.88	7.6	35.8
0.93	0.85	10.0	78.4

SIBS spectrum of $Pb(NO_3)_2$ aerosol. We used the apparatus shown schematically in Fig. 8 for the SIBS calibration experiments. It consists of the aerosol generator discussed above, high energy spark source, and detection electronics.

The spark is initiated inside the drying tube following the aerosol injector. A lens collects light at right angles to the axis defined by the two discharge electrodes, and focusses it on the entrance slit of a monochromator system with an OMA detector. In order to obtain accurate and sensitive results, the timing between the initiation of the spark and the detection of the plasma is crucial.

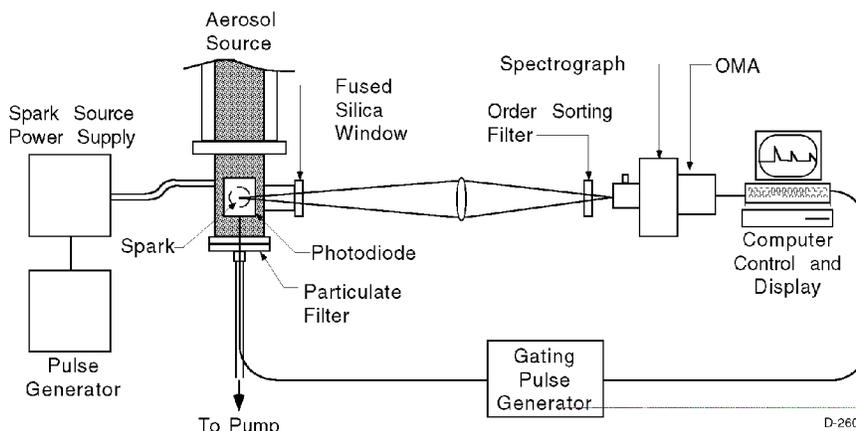


Figure 8 Schematic of system for detecting contaminants on particles

The spark generation unit is driven by a delay generator that allows the sparks to occur at set intervals. Because of the possibility of the occasional misfire or delayed sparking event, the detection system is triggered by a photodiode. Triggering from the photodiode assures that each observation takes place after an actual excitation event. When the radiation from the spark

is observed by the photodiode, an additional delay generator is activated. This generator delays the turn-on time of the OMA, so that the OMA will not be saturated by the very bright initial plasma of the spark itself. This initial bright emission is dominated by a spectral continuum arising from free electrons (bremsstrahlung radiation) present in the spark-created plasma. As the delay increases and the plasma cools, line emission from highly excited atomic and molecular species appear. These are primarily ions. As the plasma cooling continues, ions and electrons recombine and emission from neutral species of lower energy becomes more prominent.

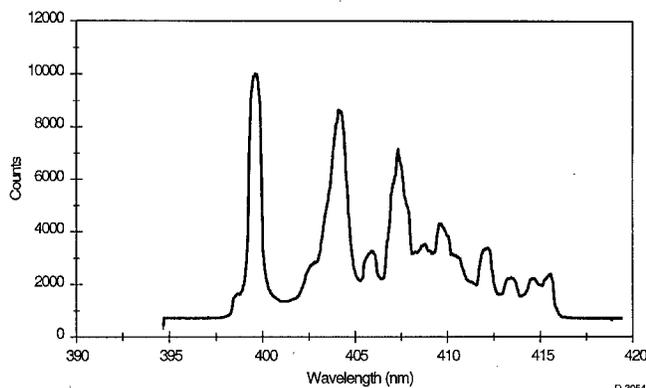


Figure 9 SIBS spectrum of Pb aerosol with no delay between spark and detection

In the final stages of cooling, which can extend past 200 μs for 5 J pulses, only emission from species of lowest internal energy persists.

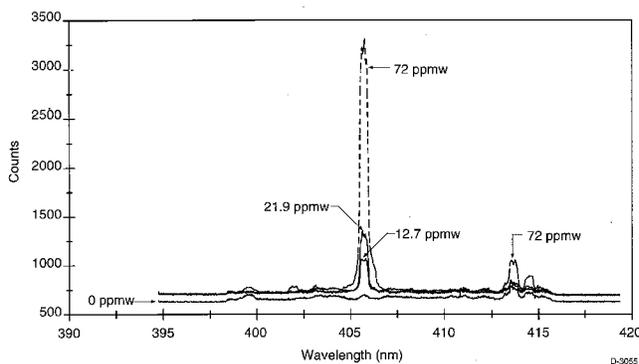


Figure 10 SIBS spectra around 406 nm at different Pb-aerosol concentrations (detection delayed 75 μs after spark).

By carefully choosing the appropriate delay between the spark ignition and the observation duration (gate), we can optimize detection conditions for a given element. The spectrum tends to simplify with longer delays after spark ignition since the emission from the higher energy species disappears. Consequently, even though total intensity is reduced, it is often useful to observe the signal at long delays after spark ignition.

Figures 9 and 10 show the spectra of lead nitrate aerosols near 405.8 nm under conditions of no delay, and with a 75 μs delay (both with a 20 μs gate), respectively. The spark produces an intense, prompt plasma, so the spectrum taken with no delay is very complex, showing many wide, unidentifiable features. Applying a delay, however, greatly simplifies the spectrum and atomic lead emissions are readily apparent. This is because the prompt emitters radiate quickly leaving only persistent metastables which can excite the atomic states. Data similar to that in Fig. 10 taken for a number of different aerosol concentrations allows us to construct a calibration curve (Fig. 11). The 3σ detection limit deduced from this curve 19 ppbw, well below the NIOSH TWA limit for lead dust (82 ppbw).

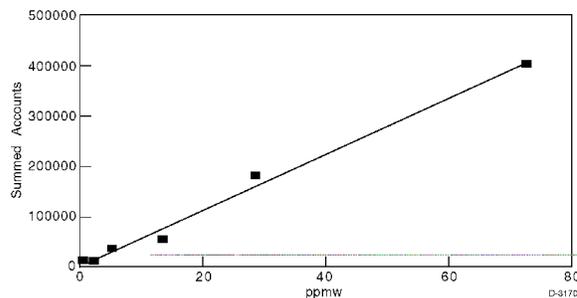


Figure 11 Calibration curve for detection of Pb aerosols by SIBS

Results to date of technology extension tasks. Table 2 summarizes the current results for the diagnostic extension tasks. The results are preliminary, and are likely to be improved with refinements in experimental technique. The most important result, we think, is the greatly improved sensitivity ANET has for lead compared to SIBS. One would expect a standard laser-induced breakdown spectroscopy (LIBS) system to have sensitivities similar to SIBS. The great improvements in sensitivity available with ANET is the reason we are currently pursuing a hybrid approach in which we use a laser to ablate and vaporize material, but do the actual detection using ANET.

Table 2. Results from Technology Extension Tasks

Detection Method	Element	Detection Sensitivity (ppbw)
ANET	Pb	0.002
	Sb	0.05
	As	0.06
	Cr	6.2
	Hg	
SIBS	Pb	10
	Cd	
	U	

We expect to finish the remaining elements in the near future, with the possible exception of Tc. Compounds of the element Tc are very strictly regulated and cannot be handled except in rigorously licensed locations. We would not be able to obtain such a license. Our plan is to test out our technique on Tc-surrogate compounds such as those containing Mn or Re. Later we will transport a portable experimental system to a location properly licensed for Tc handling and we will refine Tc detection procedures there.

Conclusions

Our results indicate that ANET is a very sensitive technique for monitoring heavy metals and chlorinated hydrocarbons. We have demonstrated an overall detection sensitivity for most species that is at or below ppb levels. ANET alone, however, appears to be most successful in treating hazardous species that have been atomized. We are therefore developing a hybrid technique which combines a miniature, solid-state laser for sample collection and vaporization with ANET for subsequent detection. This approach requires no special sample preparation, can operate continuously, and lends itself well to compact packaging.

Future Activities

The third, and final phase of the program will be to build and field test an alpha-prototype hazardous waste monitor. The fabrication will follow closely the designs developed in the current phase of the program. The alpha-prototype development will be followed by several months of testing and refinement in our laboratories. Finally, the program will conclude with an extensive series of field tests of the instrument.

At the program's conclusion, we anticipate we will transfer the technology we have developed to a manufacturing firm that is prominent in environmental monitoring and waste management. In developing our business plan we have already identified several interested firms who would be willing to take our technology to completion.

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